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ARTICLE TYPE

Self-association of oligothiophenes in isotropic systems

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The self-association equilibrium constants, K_{ass}, for the dimerization of some small oligothiophenes in acetone, acetonitrile and chloroform were measured by ^{1}H NMR spectroscopy. The gas phase interaction energies for some oligothiophene dimers were determined by computational quantum chemistry. The ^{1}H NMR results indicate that K_{ass} generally increases with chain length (number of thienyl rings, n) and solvent polarity; however, K_{ass} for thiophene ($n = 1$) was found to be higher than for the bithiophenes ($n = 2$). The linear oligothiophenes 2,2'-bithiophene and 2,2',5',2''-terthiophene were found to self-associate less than their corresponding nonlinear isomers 3,3'-bithiophene and 3,2',5',3''-terthiophene in solution and in gas phase. For α-quaterthiophene ($n = 4$) K_{ass} in solution was found to be smaller than expected. The non-linear dependence of the standard molar Gibbs energy of self-association, $\Delta_{ass}G^0_m$, with chain length in solution could be nicely reproduced and related with the conformational entropy change of dimerization. It was observed that the melting properties of oligothiophenes correlate well with their tendency to self-associate, with more self-association leading to increased liquid stability, and thus lower melting temperatures. These results highlight the relevance of self-association in isotropic systems for the correct molecular interpretation of phase equilibria.

Introduction

Oligothiophenes (OTs) and its derivatives are very important organic semiconductors (OSCs) used in several applications with significance in materials science, as for instance, conducting films, electrochromic devices, organic light-emitting diodes (OLEDs), organic field-effect transistors (OFETs), organic photovoltaic solar cells (OPVs), chemical sensors, and laser microcavities.[1-7] These materials are considered to be a promising alternative to the traditional electronic devices based on typical inorganic semiconductors. In addition, these compounds have recently found applications in areas of diagnostics, therapeutics and drug scanning.[8,9]

OTs have excellent properties such as stability under ambient conditions, structural versatility, simple and efficient synthesis, easy functionalization, and relatively low cost, which makes them one of the most studied and important classes of linear conjugated polymers.[10-12] The semiconducting properties of thiophene-based organic materials arise from the delocalization of the π electrons along the polymeric chain, which contributes for high charge mobility, a crucial asset for applications in organic electronics.[13,14] For instance, α-sexithiophene was found to present a relatively high charge mobility.[15] OTs provide interesting models for understanding the structural, electronic and thermochemical features that might control charge transport and optical properties in OSCs.

The crystal structures of several OTs have been reported in the literature.[16,17] These compounds can exhibit a variety of specific intra- and intermolecular interactions, such as π···π stacking, weak hydrogen bonds and S···S steric repulsions, which can be explored for tuning the properties of their derived materials.

Several studies have been reported on the dimerization of OTs,[18,19] their torsional behaviour,[20] and their thermodynamic properties.[21-24] Some of those studies suggest the existence of subtle factors affecting the thermodynamic stability of liquid OTs, which therefore influence their phase equilibria.[23,24] In this work the possibility that self-association in the liquid phase (formation of OTs dimers) contributes for the thermodynamic differentiation among OTs was investigated. For this purpose the self-association equilibrium constants in various solvents were measured by ^{1}H NMR spectroscopy for most of the compounds presented in figure 1. The experimental results were supported by the calculation of interaction energies for some gas phase dimers by computational chemistry methods.

This work aims to explore the self-association of oligothiophenes in isotropic systems (pure liquid and gas phases and in solution), and to understand how can self-association influence the relative phase stability of pure substances. For instance, more extensive self-association can lead to an additional stabilization of the liquid phase, which may be reflected on the properties of melting and glass transition. On the other hand, self-association can lead to some degree of organization and structuration at the nanoscale in apparently isotropic media. The existence of nanostructuration in the liquid phase has already been reported in some systems, including ionic liquids and aliphatic and aromatic hydrocarbons,[25-29] thus making the concept of phase isotropicity only fully applicable at larger scales.

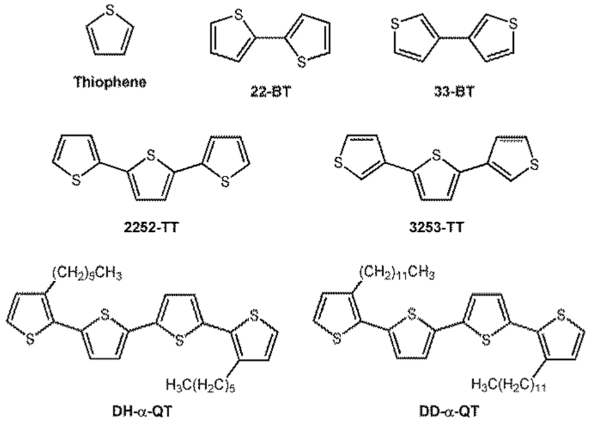

Fig. 1. The oligothiophenes studied in this work and adopted acronyms.

Experimental section

^{1}H-NMR dilution experiments

All compounds were purchased from Sigma-Aldrich and purified by recrystallization and sublimation under reduced pressure. The purity of the samples was attested by gas chromatography showing a %(m/m) purity higher than 99% in all cases. The ^{1}H NMR spectra in the selected solvents ($CDCl_3$, acetone-d_6 and acetonitrile-d_3), at $T = 295$ K, were recorded on a Bruker Avance 300 spectrometer (300.13 MHz) for various sample concentrations. The references used were TMS for $CDCl_3$ and the solvent itself for acetone-d_6 and acetonitrile-d_3. The dilution studies were carried out in the following way: 1) two or three samples of the compound are prepared in separate flasks and weighed in a Mettler AE163 balance with a resolution of 0.01 mg; 2) deuterated solvent is added to each sample with a micropipette ensuring that all the compound dissolves; 3) an aliquot of each sample is poured into the respective NMR tube with a micropipette; 4) the NMR spectrum is acquired; 5) the sample is diluted directly in the NMR tube by adding a known amount of pure deuterated solvent with a micropipette, and the NMR spectrum is recorded again; 6) step 5 is repeated for various sample concentrations. The concentrations ranged from 0.01 to 0.8 mol·dm^{-3} of oligothiophene, and were chosen to ensure a significantly large experimental interval with a balanced distribution of data points. In order to attain greater variation in chemical shift, $\Delta\delta$, with concentration high molar concentrations were preferred, taking into account the solubility limit of the compounds at $T = 295$ K in the given solvent and the reproducibility of the experimental conditions among the compounds studied. Care was taken in sample handling in order to avoid solvent evaporation and/or solute precipitation to any significant extent. The dihexyl and dodecyl derivatives, DH-α-QT and DD-α-QT respectively, were used instead of α-quaterthiophene due to the very low solubility of the later in all solvents tested. For 3253-TT K_{ass} could not be measured also due to solubility issues. The self-association equilibrium constants, K_{ass}, were determined from a non-linear fitting of the chemical shift and concentration data and assuming the equilibrium:

$$2\ \mathrm{OT\ (sln.)} \rightleftharpoons \mathrm{OT_2\ (sln.)} \qquad (1)$$

where OT represents a given oligothiophene. For each measured concentration the chemical shift, δ_{calc}, was calculated as:

$$\delta_{calc} = p(\mathrm{OT})\cdot\delta_{calc}(\mathrm{OT}) + p(\mathrm{OT_2})\cdot\delta_{calc}(\mathrm{OT_2}) \qquad (2)$$

where $\delta_{calc}(\mathrm{OT})$ and $\delta_{calc}(\mathrm{OT_2})$ are the calculated chemical shifts of pure monomer OT and dimer OT_2, respectively, and $p(\mathrm{OT})$ and $p(\mathrm{OT_2})$ are their relative equilibrium populations, calculated as: $p(\mathrm{OT}) = [\mathrm{OT}] / ([\mathrm{OT}] + [\mathrm{OT_2}])$ and $p(\mathrm{OT_2}) = 1 - p(\mathrm{OT})$, where the equilibrium concentrations [OT] and [OT_2] were computed by considering the expression of K_{eq} for equation (1) and the equation of mass balance $[\mathrm{OT}]_T = 2\cdot[\mathrm{OT_2}] + [\mathrm{OT}]$, where $[\mathrm{OT}]_T$ is the total initial concentration of the OT sample. The fitting was applied to each well-resolved aromatic peak of the compounds so as to minimize the quantity $\sum(\delta_{calc} - \delta_{obs})^2$, where δ_{obs} is the observed chemical shift at each concentration, and K_{ass} was taken as the average of all concordant values.

Computational details

All quantum chemical calculations were performed using the Gaussian 09 software package.[30] For the gas phase dimers of thiophene and the stacked parallel and anti-parallel dimers of 22-BT, 33-BT and of larger oligothiophenes (2252-TT, 3253-TT and α-quaterthiophene) the geometry optimizations and calculation of the electronic interaction energies corrected for BSSE by the counterpoise method[31,32] were performed at the B97D/6-31+G(d,p), MP2/cc-pVDZ//B97D/6-31+G(d,p) and M06-2X/6-31+G(d,p) levels of theory.[33,34] The counterpoise correction for BSSE was used throughout all the optimization procedure and in the MP2 single point energy calculations. To simulate the influence of acetone and chloroform single point energies at the B97D/6-31+G(d,p) level of theory were calculated using the Polarizable Continuum Model (PCM) as a self-consistent reaction field.[35] For the most stable thiophene, 22-BT, 2252-TT and α-quaterthiophene monomers and dimers, the zero-point energies (ZPEs) were also obtained from fundamental vibrational calculations at the B97D/6-31+G(d,p) level. To verify the influence of molecular association on the ^{1}H NMR chemical shifts, computational NMR calculations with the GIAO method[36] were performed for the most stable thiophene, 22-BT, 33-BT, 2252-TT, 3253-TT and α-quaterthiophene monomers and dimers using B97D/6-31+G(d,p). The electronic energy difference between the two stable conformers of 22-BT was calculated using the G3 computational method.[37]

Results and discussion

Self-association in solution

Figure 2 shows the ^{1}H NMR spectra of 22-BT in $CDCl_3$ and acetone-d_6 for the highest and lowest concentrations studied. Figure 3 presents the concentration dependence of chemical shifts for 22-BT in acetonitrile-d_3. The chemical shifts data is presented as $\Delta\delta = \delta(c_i) - \delta(c_{max})$, where $\delta(c_i)$ and $\delta(c_{max})$ are, respectively, the observed chemical shifts at the given sample concentration c_i and at the highest concentration studied c_{max}. Similar trends were obtained for all compounds in all solvents and the detailed results are presented as ESI. This behaviour is consistent with the formation of dimers in solution – as the concentration increases the equilibrium in eq. (1) shifts to the right; as a consequence the protons spend more time under the magnetic anisotropy effect produced by the aromatic rings of the stacked neighbouring OT molecule and the observed signals shift upfield.[38] This was also confirmed theoretically by the calculated ^{1}H chemical shifts for the monomers and dimers of all oligothiophenes studied using the B97D/6-31+G(d,p)/GIAO method – the results are presented as ESI and indicate that the average ^{1}H chemical shift of all protons in a given oligothiophene is always lower in the dimer (upfield shift) by at least 0.3 ppm.

The derived self-association equilibrium constants, K_{ass}, for each compound are presented in table 1, alongside with the standard molar Gibbs energies of self-association, calculated as $\Delta_{ass}G_m^0 = -R \cdot T \cdot \ln(K_{ass})$, where $T = 295$ K.

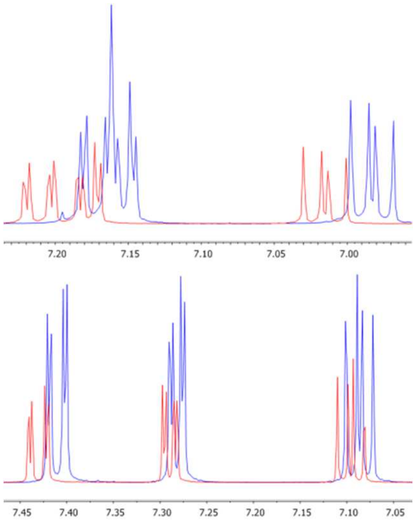

Fig. 2. ^{1}H-NMR spectra of 22-BT at the lowest (red) and highest (blue) concentrations in $CDCl_3$ (top) and acetone-d_6 (bottom).

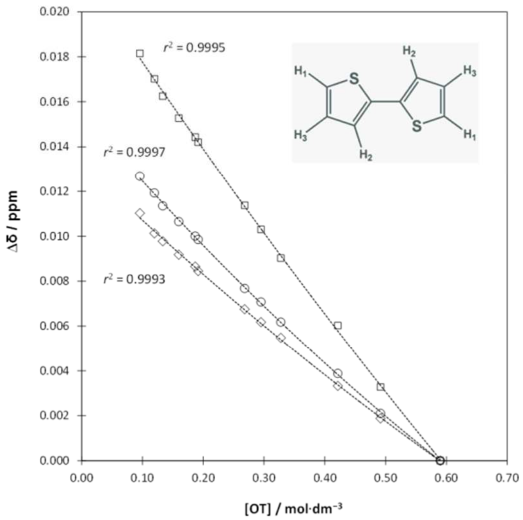

Fig. 3. The concentration dependence of chemical shifts in acetonitrile-d_3 for the three distinguishable protons of 22-BT, H_1(□), H_2(○) and H_3(◇).

The K_{ass} values are relatively small and do not ensure that the experimental errors (deriving from sample concentration, variations in the reference peaks, other contributions for Δδ, etc.) are made virtually irrelevant.[39] Although the individual results of K_{ass} can be significantly influenced by experimental errors, the trends in K_{ass} among all studied compounds are more accurate, since all measurements were conducted at the same experimental conditions, and similar trends were observed in different solvents. Moreover, polynomial fittings of $\Delta\delta = f(\text{concentration})$ with $r^2 > 0.99$ were obtained in most cases, increasing the confidence of the derived values of K_{ass}. The values of K_{ass} for DH-α-QT, DD-α-QT and α-quaterthiophene are expected to be very similar within experimental error, since the contribution of the alkyl side chains is probably of minor importance when compared to the main driving-force for self-association − the aromatic interaction between the α-QT skeletons. Moreover, self-association doesn't hinder significantly the vibrational motions of the alkyl side chains and no additional important entropic penalty shall occur on dimer formation. In fact, table 1 shows that the K_{ass} measured for DH-α-QT and DD-α-QT in $CDCl_3$ are nearly identical, thus supporting this reasoning. Also consistent with the formation of stacked dimers in solution is the fact that Δδ (as defined before) for the protons of the alkyl side chains of DH-α-QT and DD-α-QT becomes less pronounced along the alkyl chain, as the alkyl group gets further away from the interacting α-quaterthiophene units (the detailed results are presented as ESI).

Table 1. Self-association equilibrium constants, K_{ass}, and standard molar Gibbs energies, $\Delta_{ass}G_m^0$, in various solvents, at $T = 295$ K, for the oligothiophenes studied, measured by ^{1}H-NMR spectroscopy.

Compound	Solvent	K_{ass}	$\Delta_{ass}G_m^0$ / kJ·mol^{-1}
Thiophene	$CDCl_3$	0.068 ± 0.009	6.6 ± 0.3
	acetone-d_6	0.107 ± 0.040	5.5 ± 0.9
22-BT	$CDCl_3$	0.023 ± 0.002	9.3 ± 0.2
	acetone-d_6	0.046 ± 0.010	7.5 ± 0.6
	acetonitrile-d_3	0.080 ± 0.002	6.2 ± 0.1
33-BT	$CDCl_3$	0.031 ± 0.007	8.5 ± 0.6
	acetone-d_6	0.104 ± 0.008	5.6 ± 0.2
	acetonitrile-d_3	0.158 ± 0.002	4.5 ± 0.1
2252-TT	$CDCl_3$	0.128 ± 0.009	5.0 ± 0.2
	acetone-d_6	0.305 ± 0.011	2.9 ± 0.1
DH-α-QT	$CDCl_3$	0.213 ± 0.010	3.8 ± 0.1
	acetone-d_6	0.473 ± 0.061	1.8 ± 0.3
DD-α-QT	$CDCl_3$	0.222 ± 0.025	3.7 ± 0.3

The most reliable observations that can be drawn from the experimental ^{1}H NMR results presented in table 1 are:

1) 33-BT self-associates more than its isomer 22-BT in all solvents;
2) $\Delta_{ass}G_m^0$ decreases (more extensive self-association) with the increase in the solvent's dielectric constant;
3) with the exception of thiophene $\Delta_{ass}G_m^0$ decreases with increasing chain length; but that decrease is significantly more pronounced from 22-BT to 2252-TT than from 2252-TT to DH-α-QT.

The more extensive self-association (lower $\Delta_{ass}G_m^0$) of 33-BT relative to 22-BT is supported by its higher standard molar enthalpy of sublimation: $\Delta_{sub}H_m^0$, at $T = 298.15$ K, is (89.2 ± 0.3) kJ·mol^{-1} for 33-BT and (85.2 ± 0.4) kJ·mol^{-1} for 22-BT.[23] A higher cohesive energy in the solid phase is probably related with a more enthalpically favoured self-association in the dimers, with both facts reflecting the stronger intermolecular interactions in 33-BT. Entropic effects are certainly less important in differentiating between $\Delta_{ass}G_m^0$ for 22-BT and 33-BT, since in both isomers there are no special conformational restrictions in the monomer and dimer. Hence, the stronger self-association in 33-BT (lower $\Delta_{ass}G_m^0$) is likely to be enthalpically driven.

The decrease in $\Delta_{ass}G_m^0$ with increasing solvent's dielectric constant is consistent with the fact that the partial shielding of the aromatic hydrophobic π clouds in the stacked dimer avoids the necessity of a more extensive solvation by the polar solvent and thus encourages self-association.

The plot of $\Delta_{ass}G_m^0$ in $CDCl_3$ and acetone-d_6 as a function of chain length (or number of thienyl rings, *n*) for the linear oligothiophenes is presented in figure 4. The trend in $\Delta_{ass}G_m^0$ is similar for both solvents, yet the higher polar character of acetone leads to lower $\Delta_{ass}G_m^0$ (more extensive self-association). The non-linear dependence of $\Delta_{ass}G_m^0$ on chain length suggests that some enthalpic and/or entropic factors are increasing the tendency for self-association in thiophene and lowering it in α-quaterthiophene ($n = 4$) relative to the smaller homologous oligothiophenes ($n = 2, 3$). In thiophene this can be explained by a higher than expected interaction enthalpy (more negative $\Delta_{ass}H_m^0$) and/or a lower entropic penalty on binding (higher $\Delta_{ass}S_m^0$). In α-quaterthiophene it can be due to a less negative $\Delta_{ass}H_m^0$ and/or a lower $\Delta_{ass}S_m^0$. This trend also suggests that the attenuation in $\Delta_{ass}G_m^0$ with chain length can be extrapolated to larger oligothiophenes. Unfortunately, in order to test this hypothesis, $\Delta_{ass}G_m^0$ for larger oligothiophenes could not be measured due to their very low solubility.

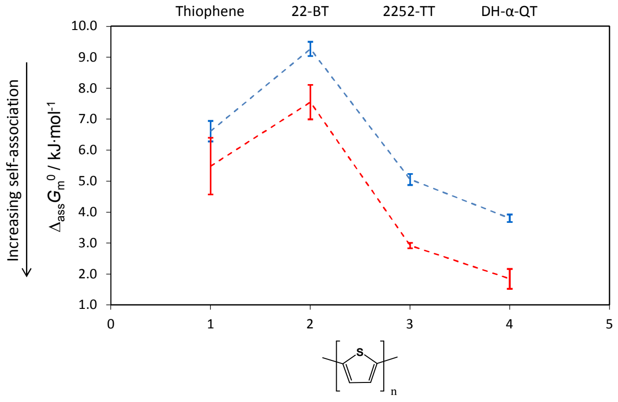

Fig. 4. Chain length dependence of the standard molar Gibbs energy of self-association for the linear α-oligothiophenes in $CDCl_3$ (blue points above) and acetone-d_6 (red points below) solutions, at $T = 295$ K. Data points are given as the corresponding error bars.

Self-association in the gas phase

The B97D/6-31+G(d,p) optimized geometries for the gas phase dimers of 22-BT and 33-BT are shown in figure 5 and the BSSE corrected electronic interaction energies, $\Delta_{int}E_m$, for all the compounds studied are presented in table 2. These energies represent the interaction energies at $T = 0$ K and are uncorrected for ZPE and for thermal contributions to enthalpy and entropy. However, $\Delta_{int}E_m$ corrected for ZPE were also calculated for the linear α-oligothiophenes. These results are presented in parenthesis in table 2 – as expected they show small quantitative differences and they follow the same qualitative trend along the series when compared with the ZPE uncorrected values. Hence, either approach will lead to the same general conclusions.

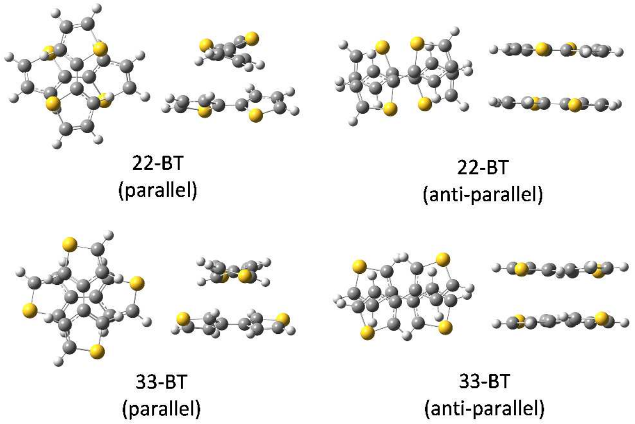

Fig. 5. B97D/6-31+G(d,p) optimized geometries for the gas phase parallel and anti-parallel bithiophene dimers.

Table 2. Electronic interaction energies, $\Delta_{int}E_m$, (corrected for BSSE and uncorrected for ZPE) calculated at the B97D/6-31+G(d,p), MP2/cc-pVDZ//B97D/6-31+G(d,p) and M06-2X/6-31+G(d,p) levels of theory for the parallel (P) and anti-parallel (AP) gas phase dimers of thiophene, the bithiophenes, the terthiophenes and α-quaterthiophene.

		$\Delta_{int}E_m$ / kJ·mol^{-1}		
Dimer		B97D [b]	MP2//B97D	M06-2X
thiophene	[a]	−12.6 (−11.0)	−10.7	−14.2
22-BT / 22-BT	P	−28.7 (−27.1)	−32.2	−38.0
	AP	−25.6	−25.2	−35.6
33-BT / 33-BT	P	−32.4	−35.9	−41.6
	AP	−29.2	−29.4	−36.8
2252-TT / 2252-TT	P	−41.2 (−37.6)	−46.5	−50.0
	AP	−39.3	−44.1	−49.3
3253-TT / 3253-TT	P	−42.4	−41.4	−48.7
	AP	−48.9	−54.1	−54.2
α-quaterthiophene	P	−56.7 (−52.3)	−65.4	−63.6
	AP	−54.2	−64.6	−67.5

[a] For thiophene $\Delta_{int}E_m$ for the strongest interacting dimer is shown; the detailed results for all the possible stable dimers are presented as ESI.
[b] The ZPE corrected $\Delta_{int}E_m$ values are shown in parenthesis.

The theoretical interaction energies presented in table 2 for the isomeric compounds are consistent with the experimental results of $\Delta_{ass}G_m^0$ and $\Delta_{sub}H_m^0$,[23] with 33-BT and 3253-TT presenting a higher tendency to self-associate than their respective isomers. By inspection of the optimized geometries of the bithiophene and terthiophene dimers this can be due to the more favoured interactions involving the outer thienyl rings in 33-BT and 3253-TT, which can better adjust the positioning of the relatively large

S atoms in order to reduce steric repulsions. The main contribution for the interaction energy in these dimers is probably from dispersion forces, which are typical of most aromatic interactions.[40-46] This also justifies the use of B97D and M06-2X, which are DFT methods capable of describing dispersive interactions.[33,34] From table 2 it can be observed that all levels of theory agree qualitatively on interaction energies, more specifically in what concerns the trends in $\Delta_{\mathrm{int}}E_{\mathrm{m}}$ along the series and the energetic differentiation between isomers and conformers. This fact supports the choice of these computational methods for the qualitative evaluation of relative interaction energies in oligothiophene dimers. As expected, $\Delta_{\mathrm{int}}E_{\mathrm{m}}$ increases (becomes more negative) with chain length, reflecting the increase in dispersion forces as the interacting π systems become larger. However, in the gas phase there are no indications that self-association is attenuated in α-quaterthiophene (the increase in $\Delta_{\mathrm{int}}E_{\mathrm{m}}$ with chain length is approximately linear), suggesting that the trend in $\Delta_{\mathrm{ass}}G_{\mathrm{m}}{}^{0}$ observed in solution (see figure 4) is entropic in nature. Moreover, $\Delta_{\mathrm{int}}E_{\mathrm{m}}$ for thiophene suggests that the reason why it self-associates significantly in solution is not related with a stronger interaction (more negative $\Delta_{\mathrm{ass}}H_{\mathrm{m}}{}^{0}$), but instead it can derive from a higher $\Delta_{\mathrm{ass}}S_{\mathrm{m}}{}^{0}$. Between the isomers 22-BT and 33-BT no significant differentiation in $\Delta_{\mathrm{ass}}S_{\mathrm{m}}{}^{0}$ is expected, and in this case the computational results for $\Delta_{\mathrm{int}}E_{\mathrm{m}}$ reproduce the experimental ones for $\Delta_{\mathrm{ass}}G_{\mathrm{m}}{}^{0}$. The interaction energies, $\Delta_{\mathrm{int}}E_{\mathrm{m}}$, were also calculated in solution state for all the dimers presented in table 2 at the B97D/6-31+G(d,p) level and considering the polarity of the solvents acetone and chloroform using the PCM method.[35] The results are presented as ESI and indicate that $\Delta_{\mathrm{int}}E_{\mathrm{m}}$ is similar in gas phase and in both solvents. Moreover, the dependence of $\Delta_{\mathrm{int}}E_{\mathrm{m}}$ on chain length is approximately linear in all cases, further supporting that the entropic contribution is the most important for bringing up the tendency observed in figure 4.

Entropic differentiation in self-association

The linear increase in $\Delta_{\mathrm{sub}}H_{\mathrm{m}}{}^{0}$ previously reported in the literature for the linear series of α-oligothiophenes (from $n = 2$ to $n = 6$)[24] and the computational results for $\Delta_{\mathrm{int}}E_{\mathrm{m}}$ presented above suggest that the interaction enthalpy, $\Delta_{\mathrm{ass}}H_{\mathrm{m}}{}^{0}$, between dimers in solution will also show an approximately linear dependence with chain length. Therefore, a differentiation in $\Delta_{\mathrm{ass}}S_{\mathrm{m}}{}^{0}$ is more likely to explain the results presented in figure 4. For instance, an entropic penalty can derive from the fact that while in 22-BT and 2252-TT all dimer conformations can stack all pairs of thienyl rings, in α-quaterthiophene some of the possible dimers, like the one shown in figure 6b, can only stack three pairs, leaving the remaining pair in a disfavoured spatial orientation for intramolecular interaction.

Smaller oligothiophenes have more conformational liberty in self-association, with various stable geometries being allowed in the formation of dimers without compromising significantly the interaction energy. The dimerization of larger units demands a more strict set of specific interaction geometries and conformations in order to maximize the interaction between all thiophene rings, which can lead to an entropically disfavoured binding. For instance, in some dimers of α-quaterthiophene only three pairs of thienyl rings can stack significantly (the other two rings are too far away and thus unable to achieve a favourable stacking interaction). As a result these conformations are less stable, and thus less populated in equilibrium than the ones that stack the four pairs of rings. This leads to lower conformational entropy, S_{conf}, of the dimer and thus lower entropy of self-association, $\Delta_{\mathrm{ass}}S_{\mathrm{m}}{}^{0}$, which contributes for higher $\Delta_{\mathrm{ass}}G_{\mathrm{m}}{}^{0}$.

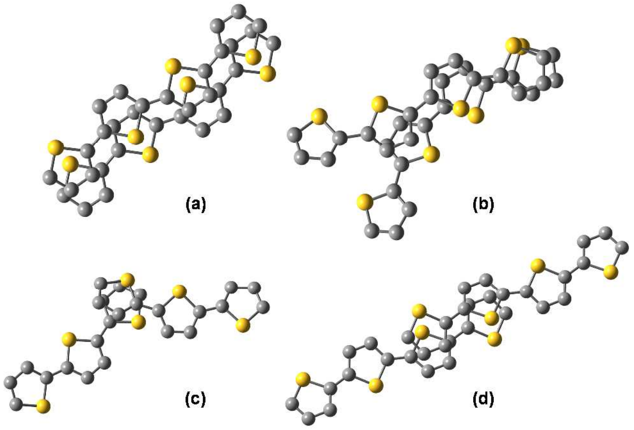

Fig. 6. Example of oligothiophene dimers with optimal (a), non-optimal (b) and partial (c, d) stacking; H atoms are omitted for clarity.

On the other hand, thiophene has more possibilities for dimer conformations, as evidenced by the work of Tsuzuki *et al.* where the authors have calculated the interaction energies for 17 different dimers.[47] Seven out of these are coplanar structures with much smaller interaction energies, and thus with a negligible weight for conformational analysis. The full geometry optimizations performed in this work for the ten remaining dimers at the B97D/6-31+g(d,p) level (with counterpoise correction for BSSE throughout all the optimization procedure), indicated that eight out of those dimer structures correspond to true minima. A potential energy surface (PES) scan was also performed for 22-BT revealing that all minima correspond to stacked dimers and none to other type of structures (e.g. T-shaped). Concerning the intramolecular conformations in monomers and dimers, while thiophene has only one stable structure, the oligothiophenes have more minima as a result of the multiple thienyl−thienyl internal rotations that can lead to non-eclipsed and eclipsed S···S configurations, as shown in figure 7.

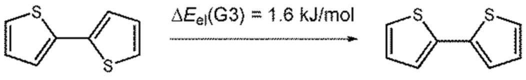

Fig. 7. Calculated energy difference, at $T = 0$ K, between the two 22-BT stable conformations (calculated by the G3 method).[37]

Following this reasoning a simple conformational analysis was employed for the estimation of the molar conformational entropies of self-association, $\Delta_{\mathrm{ass}}S_{\mathrm{m,conf}}$, for the oligothiophenes studied, according to the following equation:

$$\Delta_{\mathrm{ass}}S_{\mathrm{m,conf}} = S_{\mathrm{m,conf}}(\mathrm{dimer}) - 2 \cdot S_{\mathrm{m,conf}}(\mathrm{monomer}) \qquad (1)$$

where the molar conformational entropy, $S_{\mathrm{m,conf}}$, for the monomer and the dimer was calculated as:

$$S_{\mathrm{m,conf}} = -R \cdot \sum\{p_i \cdot \ln(p_i)\} \qquad (2)$$

where p_i is the fractional population of conformer i, calculated as:

$$p_i = \exp[\{-E_i / (R \cdot T)\} / \sum \exp\{-E_i / (R \cdot T)\}] \qquad (3)$$

and the energy of each stable monomer or dimer conformation, E_i, was calculated according to the following equation:

$$E_i = n(\text{eclipsed S}\cdots\text{S pairs}) \cdot \Delta E(\text{monomer}) + \Delta_{\mathrm{int}}E_{\mathrm{m}}(\text{oligothiophene}) \qquad (4)$$

where ΔE(monomer) = 1.6 kJ·mol^{-1} is the energy difference between the two stable monomer conformations as illustrated in figure 7, and assuming this difference additive if there are more eclipsed S atoms on larger oligothiophenes. $\Delta_{\mathrm{int}}E_{\mathrm{m}}$ was taken as the interaction energy (uncorrected for ZPE) for the dimers as follows: for thiophene the $\Delta_{\mathrm{int}}E_{\mathrm{m}}$ calculated at the B97D/6-31+g(d,p) level was used for each dimer conformation that was confirmed to be minima herein; for the oligothiophenes the average $\Delta_{\mathrm{int}}E_{\mathrm{m}}$ for the parallel and anti-parallel dimers, as presented in table 2 at the B97D/6-31+G(d,p) level, was used − for the dimers of α-quaterthiophene that only efficiently stack three rings (see figure 6b) the $\Delta_{\mathrm{int}}E_{\mathrm{m}}$ for 2252-TT was considered. The detailed conformational analysis is presented as ESI. In this analysis only the minima of the monomer and dimer states were considered, without taking into account the possibilities of partial dimerization (see figure 6c and 6d) and higher-order self-association (formation of trimers, tetramers, …). However, the significant decrease in $\Delta_{\mathrm{int}}E_{\mathrm{m}}$ for the partial dimers results in them having a negligible equilibrium population, p_i, and hence a negligible statistical weight for $S_{\mathrm{m,conf}}$(dimer); for instance $\sum p_i < 0.002$ for all the dimers of α-quaterthiophene with non-optimal stacking (see table S62 in ESI). The formation of trimers, tetramers, etc. is disfavoured by the high entropic penalty associated with the loss of translational and rotational freedom of the isolated monomers. Figure 8 presents the calculated $\Delta_{\mathrm{ass}}S_{\mathrm{m,conf}}$, at T = 295 K and expressed as $-T{\cdot}\Delta S$, for the n = 1−4 series of linear oligothiophenes. While, as mentioned before, $\Delta_{\mathrm{ass}}H_{\mathrm{m}}^{0}$ for this series is expected to be approximately linear, $\Delta_{\mathrm{ass}}S_{\mathrm{m,conf}}$ nicely follows the $\Delta_{\mathrm{ass}}G_{\mathrm{m}}^{0}$ trend observed in solution (figure 4). This suggests that the unexpectedly low $\Delta_{\mathrm{ass}}G_{\mathrm{m}}^{0}$ for thiophene can derive from its significant gain in conformational entropy on dimerization, and that the higher than expected $\Delta_{\mathrm{ass}}G_{\mathrm{m}}^{0}$ for α-quaterthiophene can be explained by the lower $\Delta_{\mathrm{ass}}S_{\mathrm{m,conf}}$ (higher $-T{\cdot}\Delta S$) when compared to 22-BT and 2252-TT.

However, as evidenced by the results presented in tables 2 and 3, it should be noted that, at least in the gas phase, the $\Delta_{\mathrm{ass}}H_{\mathrm{m}}^{0}$ term is significantly higher than $-T{\cdot}\Delta_{\mathrm{ass}}S_{\mathrm{m,conf}}$, and the prevalence of the enthalpic term, if verified, shall lead to an approximately linear $\Delta_{\mathrm{ass}}G_{\mathrm{m}} = f\{n(\text{thienyl})\}$ relation. Nevertheless, $\Delta_{\mathrm{ass}}H_{\mathrm{m}}^{0}$ is expected to be partially reduced and levelled in solution because dimerization reduces to about one half the solvent molecules that directly interact with the thienyl rings, through for instance CH···π interactions, and thus the enthalpy of solvation, $\Delta_{\mathrm{solv}}H_{\mathrm{m}}$, is expected to be more exothermic for the two monomers than for the dimer, partially cancelling $\Delta_{\mathrm{ass}}H_{\mathrm{m}}^{0}$. The levelling effect arises because as the oligothiophene becomes larger more solvent molecules are excluded from solvent-solute interactions on dimerization. The smaller and/or more levelled the $\Delta_{\mathrm{ass}}H_{\mathrm{m}}^{0}$ the more the $\Delta_{\mathrm{ass}}G_{\mathrm{m}}^{0}$ trend will resemble that of figure 8. Hence, the relative magnitude of $-T{\cdot}\Delta_{\mathrm{ass}}S_{\mathrm{m,conf}}$ might become large enough for this term to be significant and bring up the tendency observed in figure 4.

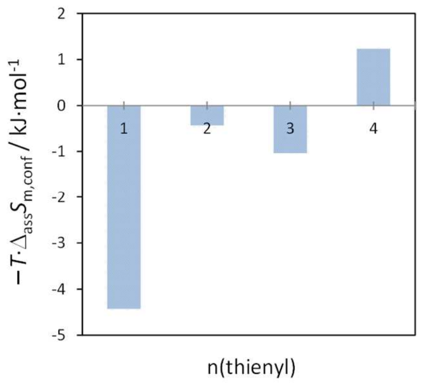

Fig. 8. Calculated molar conformational entropies of self-association, at T = 295 K and expressed as $-T{\cdot}\Delta S$, as a function of chain length for the linear α-oligothiophenes.

Self-association in the liquid phase and its influence on the melting properties of oligothiophenes

A better theoretical modelling of the liquid phase of pure oligothiophenes would require the use of molecular dynamics simulations, which fall beyond the scope of this work. However, the trends in self-association in the pure liquid oligothiophenes shall follow qualitatively those observed in solution. The difference is that the solvent becomes the oligothiophene itself and the greater or smaller tendency to self-associate will be reflected on a greater or smaller tendency of the molecules to form organized regions in the liquid, consisting of transient dimers or larger self-associated aggregates, which on average brings up some heterogeneity and structuration at the nanoscale and influences the stability of the liquid phase.[25-29] For instance, a higher tendency to self-associate in solution can be reflected on an average state of the liquid phase that has a more significant statistical contribution from local ordered structures (e.g. dimers) and a weaker character of a purely randomized liquid.

Being a phenomenon mostly observed in the liquid phase the tendency to self-associate can explain the apparent discrepancies recently reported in the literature between sublimation and fusion results for some oligothiophenes.[23,24] For instance, the standard molar enthalpies of sublimation, $\Delta_{\mathrm{sub}}H_{\mathrm{m}}^{0}$, at T = 298.15 K, are of (85.2 ± 0.4) kJ·mol^{-1} for 22-BT and of (89.2 ± 0.3) kJ·mol^{-1} for 33-BT, while the standard molar enthalpies of fusion, $\Delta_{\mathrm{fus}}H_{\mathrm{m}}^{0}$, at T = 298.15 K, are of (16.2 ± 0.1) and (15.4 ± 2.2) kJ·mol^{-1}, respectively.[23] This data indicates that the liquid phase of 33-BT is enthalpically stabilized relative to that of 22-BT, or else the higher $\Delta_{\mathrm{sub}}H_{\mathrm{m}}^{0}$ of 33-BT should be followed by a higher $\Delta_{\mathrm{fus}}H_{\mathrm{m}}^{0}$ as well. The higher tendency of 33-BT to self-associate is consistent with this fact. The more extensive association of 33-BT molecules decreases the enthalpy of the liquid phase and thus $\Delta_{\mathrm{fus}}H_{\mathrm{m}}^{0}$. This is also reflected on the entropies of phase transition. In average, more molecules are self-associated in liquid 33-BT, which leads to some loss of translational and rotational entropy, thus decreasing the standard molar entropy of fusion, $\Delta_{fus}S_m^0$, relative to 22-BT. This explains why the difference between $\Delta_{fus}S_m^0$, at T = 298.15 K, for 22-BT and 33-BT is higher than what would be predicted by the difference between their standard molar entropies of sublimation, $\Delta_{sub}S_m^0$, at T = 298.15 K.[23] Based on these results and considering equal H_m^0(g) and S_m^0(g) for 22-BT and 33-BT the relative enthalpic and entropic diagrams presented in figure 9 can be used to better visualize the effect of self-association on the phase change behaviour of bithiophenes. The factors that can differentiate between H(g) and S(g) in 22-BT and 33-BT, like extent of π conjugation or repulsive S···H interactions, are intramolecular in nature and are also reflected to a great extent in the relative stability of the solid and liquid phases. Hence, their contributions are expected to cancel out in the phase equilibria differential analysis presented in figure 9, and for this purpose is safe to assume equal H(g) and S(g) for the two isomers.

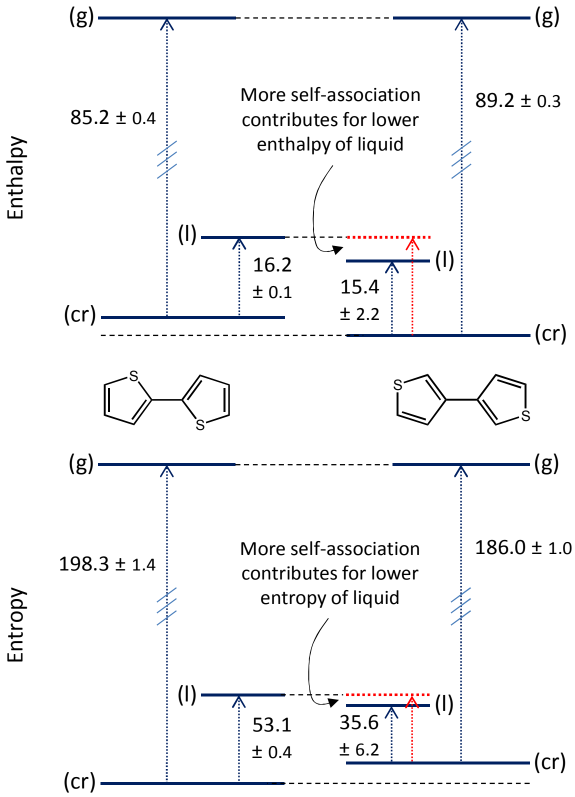

Fig. 9. Enthalpy and entropy diagrams for the fusion and sublimation of 22-BT and 33-BT. The values report $\Delta_{sub}H_m^0$ and $\Delta_{fus}H_m^0$ (kJ·mol^{-1}), and $\Delta_{sub}S_m^0$ and $\Delta_{fus}S_m^0$ (J·K^{-1}·mol^{-1}), at T = 298.15 K.[23]

A similar interpretation can be given to the phase change behaviour of 2252-TT and 3253-TT. The analogous enthalpy and entropy diagrams (see ref. 23 for details) indicate that 3253-TT has a lower enthalpy and entropy in the liquid phase than its isomer, which can also be explained by more extensive self-association. Unfortunately, due to the low solubility of this compound its K_{ass} could not be measured experimentally. However, the $\Delta_{ass}G_m^0$ observed for the analogous bithiophenes and the higher $\Delta_{sub}H_m^0$ of 3253-TT relative to 2252-TT suggest that the former is more prone to self-association, a fact that was corroborated by the computational results presented in table 2.

Another recent work focused on the study of phase stability for the series of linear oligothiophenes, from 22-BT (n = 2) to α-sexithiophene (n = 6).[24] It was observed that while there is a regular increase in $\Delta_{sub}G_m^0$ and $\Delta_{sub}H_m^0$ with the number of thienyl units along the series, the fusion data evidenced a marked increase in T_{fus} and $\Delta_{fus}H_m^0$ (like a trend change) on going from 2252-TT (n = 3) to α-quaterthiophene (n = 4), resembling somewhat the tendency shown in figure 4. The combination of the sublimation and fusion results suggests the occurrence of some destabilization of the liquid phase for the n > 3 relative to the $n \leq 3$ oligothiophenes, which can also be related with self-association. Figure 4 shows that the decrease in $\Delta_{ass}G_m^0$ in both solvents is significantly more pronounced on going from 22-BT to 2252-TT than from 2252-TT to DH-α-QT, suggesting that from this point onwards self-association will have a smaller contribution for the relative stability of the liquid phase. From 22-BT to 2252-TT the significant increase in self-association contributes substantially for stabilization of liquid 2252-TT relative to 22-BT. From 2252-TT to DH-α-QT (or α-quaterthiophene) that increase is less pronounced and self-association becomes a less important factor in differentiating between the relative stabilities of the two liquids. By being deprived of such an increase in self-association, liquid α-quaterthiophene cannot be stabilized to such an extent, and consequently the trend change in the thermodynamic melting properties emerges, with the increase in T_{fus} (an also in $\Delta_{fus}H_m^0$ and $\Delta_{fus}S_m^0$) being most pronounced from 2252-TT to α-quaterthiophene. The correlation between self-association and the melting properties for the linear α-oligothiophene series is illustrated in figures 10 and 11.

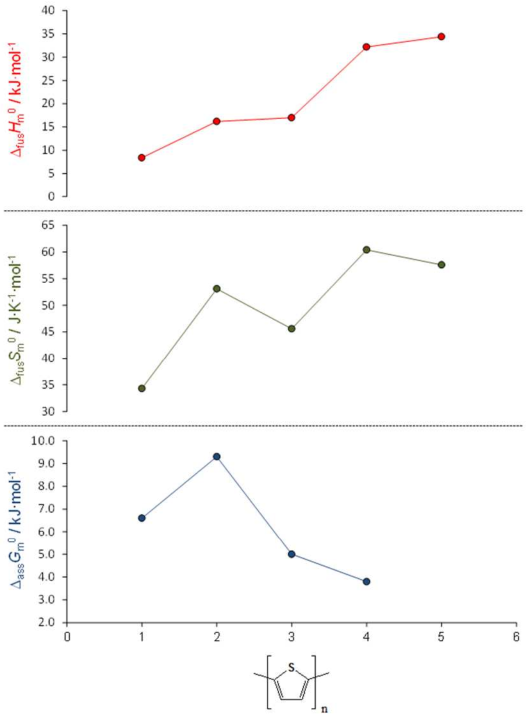

Fig. 10. Schematic comparison between $\Delta_{fus}H_m^0$,[24] $\Delta_{fus}S_m^0$,[24] and $\Delta_{ass}G_m^0$ (in $CDCl_3$) for the linear α-oligothiophene series.

Figure 10 evidences the correlation between $\Delta_{fus}H_m^0$, $\Delta_{fus}S_m^0$ and $\Delta_{ass}G_m^0$ for the linear α-oligothiophene series. It can be observed that the trends in $\Delta_{fus}H_m^0$ and $\Delta_{fus}S_m^0$ follow the trend in $\Delta_{ass}G_m^0$. For instance, the lower than expected $\Delta_{ass}G_m^0$ for thiophene indicates that it self-associates in more extent, which lowers the enthalpy and entropy of the liquid phase and is reflected in a decrease of $\Delta_{fus}H_m^0$ and $\Delta_{fus}S_m^0$, as observed. Moreover, the significant increase in $\Delta_{fus}H_m^0$ and $\Delta_{fus}S_m^0$ for α-quaterthiophene is nicely accompanied by a not so sharp decrease in $\Delta_{ass}G_m^0$. The trend change at α-quaterthiophene in $\Delta_{ass}G_m^0$ and T_{fus} can also be visualized in figure 11, suggesting that the main reason for the sharp increase in T_{fus} from $n = 3 \rightarrow 4$ is the lower than expected tendency of α-quaterthiophene, when compared to the smaller oligomers, to self-associate in the liquid phase. It is also worth noting that thiophene has a slightly lower T_{fus} than the extrapolation from 22-BT and 2252-TT would predict;[24,48] a fact that correlates well with its higher than expected tendency to self-associate.

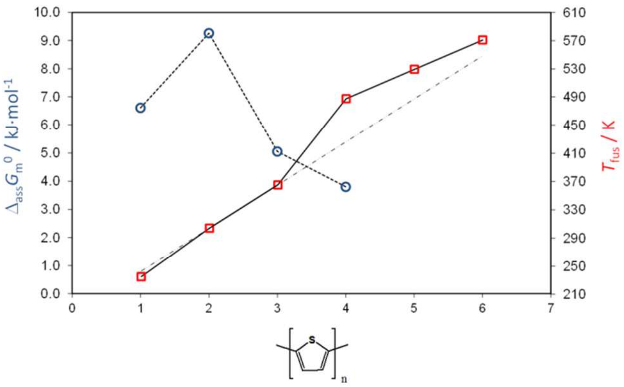

Fig. 11. Schematic comparison between $\Delta_{ass}G_m^0$ (in $CDCl_3$) (○) and T_{fus} (□)[24] for the linear α-oligothiophene series, evidencing the trend change at $n = 3 \rightarrow 4$ in both correlations. The dotted line represents the expected trend in T_{fus} if $\Delta_{ass}G_m^0$ showed a linear correlation with chain length.

If $\Delta_{ass}G_m^0$ was to decrease monotonously with chain length a more linear increase in T_{fus} along the whole $n = 1 \rightarrow 6$ series could be expected. In this perspective self-association can be regarded as an additional factor that influences the melting properties in a less monotonous and predictable way (like, for example, when compared with the effect of molecular size) and shapes their trends along the series. In a pure thermodynamic perspective, taking into account that at T_{fus}, $\Delta_{fus}G_m = 0$ and hence $T_{fus} = \Delta_{fus}H_m / \Delta_{fus}S_m$, the influence of self-association on melting can be pictured as two opposing effects: more self-association decreases $H_m^0(l)$ and hence $\Delta_{fus}H_m$, thus lowering T_{fus}, but it lowers $S_m^0(l)$ and hence $\Delta_{fus}S_m$, thus increasing T_{fus}. However, for the liquid phase to present some degree of self-association this must be thermodynamically reflected on a decrease of $G_m^0(l)$ relative to the same liquid without self-association. Hence, the net effect of self-association is always to increase the stability of the liquid and consequently decrease its T_{fus}. If the minimum in $G_m^0(l)$ is reached for a higher degree of self-association the liquid can reach lower values of $G_m^0(l)$ and therefore present a more pronounced decrease of T_{fus}.

These results indicate the existence of a significant relationship between self-association and phase equilibria. The crucial reason for the observed behaviour in the self-association and melting properties of α-oligothiophenes is probably the decrease in conformational entropy of the dimer as the chain length grows, due to the fact that the dimerization of larger units demands a more strict set of specific conformations in order to maximize the interaction between all thienyl rings. In principle, many different substances can self-associate to some extent in their pure liquid and gaseous phases, since equal molecules have the tendency, some more than others, to favourably interact with themselves. However, self-association is generally entropically disfavoured due to the significant loss of translational, rotational and in some cases vibrational entropy on dimer formation. Hence, for self-association to be significant this entropic penalty must either be reduced or compensated by a large interaction enthalpy. This can happen when one or more of the following conditions are observed: 1) the interacting systems are rigid molecules, thus reducing the vibrational entropy loss; 2) the dimer has large conformational entropy; 3) self-association is strong enough in order to overcome the entropic penalty. For instance, in carboxylic acids and ionic liquids the formation of, respectively, hydrogen bonded dimers and ion pairs more than compensates for the entropic penalty on self-association, and in fact these substances tend to form interacting aggregates (dimers or more complex aggregates) in the liquid and/or gas phases,[25-28,49-56] thus leading to significant nanostructuration in the so-called isotropic phase. In the particular case of the oligothiophenes studied herein there is a more subtle interplay of factors. The aromatic interaction enthalpy, although usually not as strong as the interactions in carboxylic acids and ionic liquids, is also substantial – it is important to keep in mind that, contrary to ionic interactions in ionic liquids and hydrogen bonds in carboxylic acids, which depend more drastically on the relative orientation of the interacting species, aromatic interactions, which can indeed be very strong in large systems, have a smoother potential energy surface, and so a significant fraction of the interaction energy can be recovered in the randomized liquid. Moreover, the reduced conformational freedom of oligothiophene molecules and the many possible conformations of the dimer state lead to a generally positive $\Delta_{ass}S_{m,conf}$, thus contributing for a lower entropic penalty. The combination of these factors leads to a degree of self-association in the liquid that is significant enough in order to produce observable changes on the melting properties of these compounds.

The same reasoning on self-association can also be applied to the gas phase. However, due to the larger entropic penalty associated with the formation of the dimer in the gas than in the liquid or solution, self-association in the gas only becomes significant when $\Delta_{ass}H_m^0$ is relatively high, as for example in the case of carboxylic acids,[49,51-53] and/or when the equilibrium vapour pressure, p_{eq}, is high enough in order to shift the gas phase self-association equilibrium towards formation of the dimer. In these cases self-association also influences the stability of the gas phase and with it the sublimation and vaporization equilibria, affecting important properties like T_{boil} and p_{eq}.

Conclusions

In this work, the self-association equilibrium constants, K_{ass}, and the corresponding Gibbs energies of self-association, $\Delta_{\mathrm{ass}}G_{\mathrm{m}}^{0}$, for some oligothiophenes in solution were determined experimentally by means of ^{1}H NMR spectroscopy. According to what was expected for the self-association of aromatic hydrophobic molecules K_{ass} was found to increase with the increase in solvent polarity. However, the dependence of K_{ass} on chain length didn't entirely follow the expected behaviour, with thiophene self-associating more than the bithiophenes and α-quaterthiophene presenting a lower than expected K_{ass}. The support of computational chemistry indicated that, while $\Delta_{\mathrm{ass}}H_{\mathrm{m}}^{0}$ seems to follow an approximately linear dependence with chain length, which is also consistent with the observed trend in $\Delta_{\mathrm{sub}}H_{\mathrm{m}}^{0}$, the non-linear dependence of $\Delta_{\mathrm{ass}}G_{\mathrm{m}}^{0}$ with chain length is well reproduced by the calculated conformational entropy change of self-association, $\Delta_{\mathrm{ass}}S_{\mathrm{m,conf}}$. According to the global results presented herein more self-association in oligothiophenes was found to be related with an increased stability of the liquid phase, thus influencing the thermodynamic properties of fusion and ultimately contributing to a decrease of the melting temperatures. This work evidences how self-association in isotropic systems can have a noticeable influence on the thermodynamic properties of organic substances, and in some cases lead to important energetic differentiation between interrelated compounds. Therefore, whenever a system presents the possibility to self-associate in a significant extent this may lead to the occurrence of nanostructuration within an otherwise purely isotropic phase and that must be considered for the correct evaluation of the properties of that particular phase and for the correct molecular interpretation of phase equilibria.

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